

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
28 June 2001 (28.06.2001)

PCT

(10) International Publication Number
WO 01/46339 A2(51) International Patent Classification⁷: C10G 2/00,
C07C 6/00, C10M 175/00

(21) International Application Number: PCT/US00/33950

(22) International Filing Date:
15 December 2000 (15.12.2000)

(25) Filing Language: English

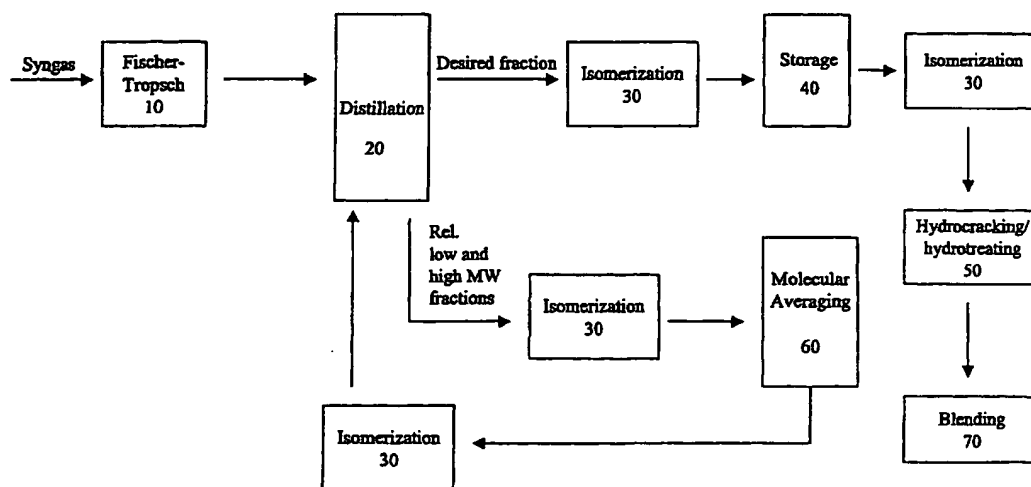
(26) Publication Language: English

(30) Priority Data:
09/469,574 22 December 1999 (22.12.1999) US(71) Applicant: CHEVRON U.S.A. INC. [US/US]; 3rd Floor,
2613 Camino Ramon, San Ramon, CA 94583-4289 (US).(72) Inventors: O'REAR, Dennis, J.; 40 Upland Drive,
Petaluma, CA 94952 (US). KRUG, Russell; 44 Olympia
Way, Novato, CA 94949 (US).(74) Agents: AMBROSIUS, James, W. et al.; Chevron Corpo-
ration, Law Dept., P.O. Box 6006, San Ramon, CA 94583-
0806 (US).(81) Designated States (*national*): AE, AL, AM, AT, AU, AZ,
BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE,
DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID,
IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT,
LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL,
PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ,
UA, UG, VN, YU, ZA, ZW.(84) Designated States (*regional*): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,
IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF,
CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

— Without international search report and to be republished
upon receipt of that report.For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: SYNTHESIS OF NARROW LUBE CUTS FROM FISCHER-TROPSCH PRODUCTS



(57) Abstract: A process for preparing hydrocarbons in the lube base oil range, lube base oils and lube oil compositions from a fraction with an average molecular weight above a target molecular weight and a fraction with an average molecular weight below a target molecular weight via molecular averaging is described. The fractions can be obtained, for example, from Fischer-Tropsch reactions, and/or obtained from the distillation of crude oil. Molecular averaging converts the fractions to a product with a desired molecular weight, for use in preparing a lube oil composition. The product can optionally be isomerized to lower the pour point, and also can be blended with suitable additives for use as a lube oil composition.

1 **SYNTHESIS OF NARROW LUBE CUTS**
2 **FROM FISCHER-TROPSCH PRODUCTS**

3
4 RELATED APPLICATION

5
6 This application is related to "Process for Conversion of Natural Gas and
7 Associated Light Hydrocarbons to Salable Products" by Dennis J. O'Rear,
8 Charles L. Kibby and Russell R. Krug, filed concurrently with this application.
9

10 FIELD OF THE INVENTION

11
12 This invention relates to the molecular averaging of various feedstocks to form
13 lube oils.
14

15 BACKGROUND OF THE INVENTION

16
17 There is a need for lubricating oils in the C₃₀+ range which have a high
18 viscosity index (VI) and good oxidation stability. The majority of lubricating
19 oils used in the world today are derived from crude oil, and include a
20 petroleum base oil and an additive package. The base oils are refined from
21 crude oil through a plurality of processes such as distillation, hydrocracking,
22 hydroprocessing, catalytic dewaxing, and the like. Hydrocarbons in the lube
23 oil boiling range from these processes needs to be further processed to create
24 the finished base oil. In creating the base oil, the refiner desires to obtain the
25 highest possible yield while preserving the VI of the oil.
26

27 Crude oil fractions in the C₃₀+ range often tend to include waxes. Since the
28 presence of wax in lube oil adversely affects various physical properties, such
29 as the pour point and cloud point, the waxy components are typically
30 removed. The waxy components of the oil can be removed using various
31 processes, including solvent dewaxing and/or catalytic dewaxing, both of

1 which tend to provide lower yields at a given VI. It would be highly desirable
2 to have a process that optimizes the yield of lube oil at a given VI.

3

4 The use of crude oil as a feedstock for preparing lube oils is limited by the
5 product loss associated with the steps required to remove the waxy
6 components. Further, crude oil is in limited supply, it includes aromatic
7 compounds believed to cause cancer, and contains sulfur and nitrogen-
8 containing compounds that can adversely affect the environment.

9

10 Lube oils can also be prepared from natural gas. This involves converting
11 natural gas, which is mostly methane, to synthesis gas (syngas), which is a
12 mixture of carbon monoxide and hydrogen, and subjecting the syngas to
13 Fischer-Tropsch reaction conditions. An advantage of using fuels prepared
14 from syngas is that they do not contain significant amounts of nitrogen or
15 sulfur and generally do not contain aromatic compounds. Accordingly, they
16 have minimal health and environmental impact.

17

18 A limitation associated with Fischer-Tropsch chemistry is that it tends to
19 produce a broad spectrum of products, ranging from methane to wax. While
20 the product stream includes a fraction useful as lube oils, it is not the major
21 product. Product slates for syngas conversion over Fischer-Tropsch catalysts
22 (for example, Fe, Co and Ru) are controlled by polymerization kinetics with
23 fairly constant chain growth probabilities that fix the possible product
24 distributions. Heavy products with a relatively high selectivity for wax are
25 produced when chain growth probabilities are high. Methane is produced with
26 high selectivity when chain growth probabilities are low.

27

28 It is generally possible to isolate various fractions from a Fischer-Tropsch
29 reaction, for example, by distillation. The fractions include, among others, a
30 gasoline fraction (B.P. about 68-450°F/20-232°C), a middle distillate fraction
31 (B.P. about 250-750°F/121-399°C), a wax fraction (B.P. about

1 650-1200°F/343-649°C) primarily containing C₂₀ to C₅₀ normal paraffins with a
2 small amount of branched paraffins and a heavy fraction (B.P. above about
3 1200°F/649°C) and tail gases. A suitable fraction for use in preparing a lube
4 oil can be isolated from the product stream by distillation. However,
5 depending on market considerations, it might be advantageous to provide a
6 process that would convert the other fractions into fractions suitable for use in
7 preparing lube oils. The present invention provides such a process.

8

9

SUMMARY OF THE INVENTION

10

11 In its broadest aspect, the present invention is directed to an integrated
12 process for producing hydrocarbons in the lube base oil range, lube base oils
13 and lube oils. As used herein, lube base oils are generally combined with an
14 additive package to provide finished lube oils. Hydrocarbons in the lube base
15 oil range are prepared via molecular averaging of a relatively low molecular
16 weight fraction and a relatively high molecular weight fraction.

17

18 The resulting hydrocarbons tend to be waxy unless they are isomerized prior
19 to the molecular averaging step. Isomerization of the hydrocarbons provides
20 a lube base oil, which, when combined with the additive package, provides a
21 lube oil composition. Catalytic isomerization improves the pour point and
22 viscosity index. Hydrotreatment can optionally be performed on the
23 hydrocarbons or lube base oil to hydrotreatment to remove olefins,
24 oxygenates and other impurities.

25

26 Depending on the desired physical and chemical properties of the lube oil
27 composition, the product of the molecular averaging reaction can include
28 virtually any combination of hydrocarbons between C₂₀ and C₅₀. Preferably,
29 the lube oil composition includes mostly hydrocarbons in the range of around
30 C₃₀. When preparing a lube base oil composition in the C₂₀ to C₅₀ range, one
31 can combine hydrocarbon materials below C₂₀ and above C₅₀ and subject

1 them to molecular averaging to arrive at a composition in the desired range.
2 When preparing a lube base oil composition in the C₃₀ range, for example, C₂₀
3 and C₄₀ fractions can be combined and subjected to molecular averaging.
4
5 In one embodiment, the process involves performing Fischer-Tropsch
6 synthesis on syngas to provide a range of products, isolating various fractions
7 via fractional distillation, and performing molecular averaging on a relatively
8 low molecular weight fraction and a relatively high molecular weight fraction to
9 provide a product with a molecular weight between the low and high
10 molecular weights, which is suitable for use in preparing a lube base oil
11 composition. In another embodiment, relatively low molecular weight and/or
12 relatively high molecular weight fractions are obtained from another source,
13 for example, via distillation of crude oil, provided that the fractions do not
14 include appreciable amounts (i.e., amounts which would adversely affect the
15 catalyst used for molecular averaging) of thiols, amines, or cycloparaffins.
16
17 It may be advantageous to take representative samples of each fraction and
18 subject them to molecular averaging reactions, adjusting the relative
19 proportions of the fractions until a product with desired properties is obtained.
20 Then, the reaction can be scaled up using the relative ratios of each of the
21 fractions that resulted in the desired product. Using this method, one can "dial
22 in" a molecular weight distribution which can be roughly standardized between
23 batches and result in a reasonably consistent product.

24 BRIEF DESCRIPTION OF THE DRAWING

25
26
27 The Figure is a schematic flow diagram representing one embodiment of the
28 invention.
29

1 DETAILED DESCRIPTION OF THE INVENTION

2

3 In its broadest aspect, the present invention is directed to an integrated
4 process for producing hydrocarbons in the lube base oil range, lube base oils
5 and lube oils via molecular averaging of relatively low molecular weight and
6 relatively high molecular weight fractions, for example, C₂₀ and C₄₀ fractions.
7 The lube base oil composition includes hydrocarbons in the range of between
8 about C₂₀ and C₅₀, but is preferably around C₃₀.

9

10 As used herein, "hydrocarbons in the lube base oil range" are hydrocarbons
11 having a boiling point in the lube oil range (i.e., between 650°F and 1200°F).
12 As used herein, a "relatively low molecular weight fraction" is a fraction with
13 an average molecular weight lower than the average molecular weight of the
14 desired lube oil composition. A "relatively high molecular weight fraction" is a
15 fraction with an average molecular weight higher than the average molecular
16 weight of the desired lube oil composition. "Average molecular weight" is
17 molar average molecular weight. Preferably, the relatively high and relatively
18 low molecular weight fractions are each within about 10 carbons from that of
19 the desired product. However, the process described herein can tolerate
20 broader differences in molecular weight.

21

22 An important consideration for determining an appropriate ratio of high
23 molecular weight and low molecular weight fractions is that the average
24 molecular weight of the two fractions, taking into consideration the relative
25 proportions of each fraction, is close to the desired average molecular weight.
26 Because of reactivity differences, it is possible to have an excess of one
27 component, in particular, the lower molecular weight fraction.

28

29 In one embodiment, the process involves performing Fischer-Tropsch
30 synthesis on syngas to provide a range of products, isolating various fractions
31 via fractional distillation (including relatively high and relatively low molecular

1 weight fractions), and performing molecular averaging on the relatively low
2 molecular weight and relatively high molecular weight fractions. Alternatively,
3 the relatively low molecular weight and/or relatively high molecular weight
4 fractions are obtained from another source, for example, via distillation of
5 crude oil, provided that the fractions do not include an appreciable amount of
6 olefins, heteroatoms or saturated cyclic compounds.

7
8 The product from the molecular averaging reaction typically includes
9 hydrocarbons with molecular weights between the low and high molecular
10 weights. A suitable fraction can be isolated, for example, by distillation, which
11 fraction contains hydrocarbons in the lube base oil range. These
12 hydrocarbons generally are waxy solids, but can be readily isomerized to form
13 a lube base oil composition. The lube base oil composition can be blended
14 with suitable additives to form the lube base oil composition.

15
16 The process described herein is an integrated process. As used herein, the
17 term "integrated process" refers to a process which involves a sequence of
18 steps, some of which may be parallel to other steps in the process, but which
19 are interrelated or somehow dependent upon either earlier or later steps in the
20 total process.

21
22 An advantage of the present process is the effectiveness with which the
23 present process may be used to prepare high quality base oils useful for
24 manufacturing lubricating oils, and particularly with feedstocks which are not
25 conventionally recognized as suitable sources for such base oils.

26
27 Lube Base Oil Composition

28
29 The lube base oil prepared according to the process described herein can
30 have virtually any desired molecular weight, depending on the desired
31 physical and chemical properties of the lube oil composition, for example,
32 pour point, viscosity index and the like. The molecular weight can be

1 controlled by adjusting the molecular weight and proportions of the high
2 molecular weight and low molecular weight fractions. Lube oil compositions
3 with boiling points in the range of between about 650°F and 1200°F are
4 preferred, with boiling points in the range of between about 700°F and 1100°F
5 being more preferred. The currently most preferred average molecular weight
6 is around C₃₀, which has a boiling point in the range of roughly 840°F,
7 depending on the degree of branching. However, the process is adaptable to
8 generate higher molecular weight lube oils, for example, those in the C₃₅-C₄₀
9 range, or lower molecular weight lube oils, for example, those in the C₂₀-C₂₅
10 range. Preferably, the majority of the composition includes compounds within
11 about 8 carbons of the average, more preferably, within around 5 carbons of
12 the average.

13
14 In a preferred embodiment, the composition includes branched hydrocarbons.
15 The products of the Fischer-Tropsch synthesis tend to be linear, which can
16 result in a relatively high pour point. However, the linear products can be
17 isomerized readily using known isomerization chemistry, or, alternatively, the
18 reactants subjected to molecular averaging can be isomerized before the
19 molecular averaging step. Accordingly, the preferred lube base oil
20 composition can generally be described as including hydrocarbons in the
21 C₂₀-C₅₀, preferably around C₃₀ range which include branching typical of that
22 observed in compositions subjected to catalytic dewaxing and/or
23 isomerization dewaxing processes.

24
25 The lube base oil and/or lube oil preferably have a pour point in the range of
26 10°C or lower, more preferably 0°C or lower, still more preferably, -15°C or
27 lower, and most preferably, between -15°C and -40°C. The degree of
28 branching in the composition is preferably kept to the minimum amount
29 needed to arrive at the desired pour point. Pour point depressants can be
30 added to adjust the pour point to a desired value.

31

1 The lube base oil and/or lube oil composition preferably have a kinematic
2 viscosity of at least 3 centistokes, more preferably at least 4 centistokes, still
3 more preferably at least 5 centistokes, and most preferably at least
4 6 centistokes, where the viscosity is measured at 40°C. They also have a
5 viscosity index (a measure of the resistance of viscosity change to changes in
6 temperature) of at least 100, preferably 140 or more, more preferably over
7 150, and most preferably over 160.

8
9 Another important property for the lube base oil and lube oil composition is
10 that it has a relatively high flash point for safety reasons. Preferably, the flash
11 point is above 90°C, more preferably above 110°C, still more preferably
12 greater than 175°C, and most preferably between 175°C and 300°C. The
13 following table (Table 1) shows a correlation between viscosity and flash point
14 of preferred lubricants for use in automobiles.

15
16 Table 1

Viscosity at 40°C (cSt)	Flash Point (D93), °C	Flash Point (D92), °C
3.0	175	175
4.08	205	208
4.18	201	214
6.93	230	237
11.03	251	269

17
18 *D92 and D93 listed in the above table refer to ASTM tests for measuring
19 flash point:

20
21 Flash Point, COC, °C D 92
22 Flash Point, PMCC, °C D 93

23

24 The lube oil can be used, for example, in automobiles. The high paraffinic
25 nature of the lube oil gives it high oxidation and thermal stability, and the lube
26 oil has a high boiling range for its viscosity, i.e., volatility is low, resulting in
27 low evaporative losses.

1 The lube oil can also be used as a blending component with other oils. For
2 example, the lube oil can be used as a blending component with
3 polyalphaolefins, or with mineral oils to improve the viscosity and viscosity
4 index properties of those oils, or can be combined with isomerized petroleum
5 wax. The lube oils can also be used as workover fluids, packer fluids, coring
6 fluids, completion fluids, and in other oil field and well-servicing applications.
7 For example, they can be used as spotting fluids to unstick a drill pipe that
8 has become stuck, or they can be used to replace part or all of the expensive
9 polyalphaolefin lubricating additives in downhole applications. Additionally,
10 they can also be used in drilling fluid formulations where shale-swelling
11 inhibition is important, such as those described in U.S. Pat. No. 4,941,981 to
12 Perricone et al.

13
14 Preferably, the lube oil is obtained via molecular averaging of Fischer-Tropsch
15 products and, therefore, contains virtually no heteroatoms or saturated cyclic
16 compounds. Alternatively, the lube oil can be obtained by molecular
17 averaging of other feedstocks, preferably in which at least the heteroatoms,
18 and more preferably the saturated cyclic compounds, have been removed.

19

20 Additives

21

22 The lube oil composition includes various additives, such as lubricants,
23 emulsifiers, wetting agents, densifiers, fluid-loss additives, viscosity modifiers,
24 corrosion inhibitors, oxidation inhibitors, friction modifiers, demulsifiers,
25 anti-wear agents, dispersants, anti-foaming agents, pour point depressants,
26 detergents, rust inhibitors and the like. Other hydrocarbons, such as those
27 described in U.S. Patent No. 5,096,883 and/or U.S. Patent No. 5,189,012,
28 may be blended with the lube oil provided that the final blend has the
29 necessary pour point, kinematic viscosity, flash point, and toxicity properties.
30 The total amount of additives is preferably between 1-30 percent. All
31 percentages listed herein are weight percentages unless otherwise stated.

32

1 Examples of suitable lubricants include polyol esters of C₁₂-C₂₈ acids.

2

3 Examples of viscosity modifying agents include polymers such as ethylene
4 alpha-olefin copolymers which generally have weight average molecular
5 weights of from about 10,000 to 1,000,000 as determined by gel permeation
6 chromatography.

7

8 Examples of suitable corrosion inhibitors include phosphosulfurized
9 hydrocarbons and the products obtained by reacting a phosphosulfurized
10 hydrocarbon with an alkaline earth metal oxide or hydroxide.

11

12 Examples of oxidation inhibitors include antioxidants such as alkaline earth
13 metal salts of alkylphenol thioesters having preferably C₅-C₁₂ alkyl side chain
14 such as calcium nonylphenol sulfide, barium t-octylphenol sulfide,
15 dioctylphenylamine, as well as sulfurized or phosphosulfurized hydrocarbons.
16 Additional examples include oil soluble antioxidant copper compounds such
17 as copper salts of C₁₀ to C₁₈ oil soluble fatty acids.

18

19 Examples of friction modifiers include fatty acid esters and amides, glycerol
20 esters of dimerized fatty acids and succinate esters or metal salts thereof.

21

22 Dispersants are well known in the lubricating oil field and include high
23 molecular weight alkyl succinimides being the reaction products of oil soluble
24 polyisobutylene succinic anhydride with ethylene amines such as
25 tetraethylene pentamine and borated salts thereof.

26

27 Pour point depressants such as C₈-C₁₈ dialkyl fumarate vinyl acetate
28 copolymers, polymethacrylates and wax naphthalene are well known to those
29 of skill in the art.

30

31 Examples of anti-foaming agents include polysiloxanes such as silicone oil
32 and polydimethyl siloxane; acrylate polymers are also suitable.

1

2 Examples of anti-wear agents include zinc dialkyldithiophosphate, zinc diaryl
3 diphosphate, and sulfurized isobutylene.

4

5 Examples of detergents and metal rust inhibitors include the metal salts of
6 sulfonic acids, alkylphenols, sulfurized alkylphenols, alkyl salicylates,
7 naphthenates and other oil soluble mono and dicarboxylic acids such as
8 tetrapropyl succinic anhydride. Neutral or highly basic metal salts such as
9 highly basic alkaline earth metal sulfonates (especially calcium and
10 magnesium salts) are frequently used as such detergents. Also useful is
11 nonylphenol sulfide. Similar materials made by reacting an alkylphenol with
12 commercial sulfur dichlorides. Suitable alkylphenol sulfides can also be
13 prepared by reacting alkylphenols with elemental sulfur. Also suitable as
14 detergents are neutral and basic salts of phenols, generally known as
15 phenates, wherein the phenol is generally an alkyl substituted phenolic group,
16 where the substituent is an aliphatic hydrocarbon group having about 4 to 400
17 carbon atoms.

18

19 Antioxidants can be added to the lube oil to neutralize or minimize oil
20 degradation chemistry. Examples of antioxidants include those described in
21 U.S. Pat. No. 5,200,101, which discloses certain amine/hindered phenol, acid
22 anhydride and thiol ester-derived products.

23

24 The combination of a metallic dithiophosphate hydroperoxide decomposer
25 and aminic antioxidant is reported to have a synergistic effect on lubricant
26 antioxidant performance. See Maleville et al., *Lubrication Science*, V9, No. 1,
27 pg. 3-60 (1996). Sulfur-substituted derivatives of mercapto carboxylic esters
28 also are reported to possess antioxidant properties. See M. A. Mirozopeva
29 et al., *Naftekhimiya*, V28, No. 6, pg. 831-837 (1988).

30

31 Additional lube oils additives are described in U.S. Patent No. 5,898,023 to
32 Francisco et al., the contents of which are hereby incorporated by reference.

1 Feedstocks for the Molecular Averaging Reaction

2
3 Examples of feedstocks that can be molecularly averaged in accordance with
4 the present invention include oils that generally have relatively high pour
5 points which it is desired to reduce to relatively low pour points. Numerous
6 petroleum feedstocks, for example, those derived from crude oil, are suitable
7 for use. Examples include petroleum distillates having a normal boiling point
8 above about 100°C, gas oils and vacuum gas oils, residuum fractions from an
9 atmospheric pressure distillation process, solvent-deasphalted petroleum
10 residues, shale oils, cycle oils, petroleum and slack wax, waxy petroleum
11 feedstocks, NAO wax, and waxes produced in chemical plant processes.
12 Straight chain n-paraffins either alone or with only slightly branched chain
13 paraffins having 16 or more carbon atoms are sometimes referred to herein
14 as waxes.

15
16 The feedstocks should not include appreciable amounts of olefins,
17 heteroatoms, or saturated cyclic compounds. Preferred feedstocks are
18 products from Fischer-Tropsch synthesis or waxes from petroleum products.
19 If any heteroatoms, olefins or saturated cyclic compounds are present in the
20 feedstock, they should be removed before the molecular averaging reaction.
21 Olefins and heteroatoms can be removed by hydrotreating. Saturated cyclic
22 hydrocarbons can be separated from the desired feedstock paraffins by use of
23 adsorption with molecular sieves or by deoiling or by complexing with urea.

24
25 Preferred petroleum distillates for use in the relatively low molecular weight
26 fraction boil in the normal boiling point range of 200°C to 700°C, more
27 preferably in the range of 260°C to 650°C. Suitable feedstocks also include
28 those heavy distillates normally defined as heavy straight-run gas oils and
29 heavy cracked cycle oils, as well as conventional FCC feed and portions
30 thereof. Cracked stocks may be obtained from thermal or catalytic cracking of
31 various stocks. The feedstock may have been subjected to a hydrotreating

THIS PAGE BLANK (USPTO)